Late metal diphosphinosulfinyl $S(O)P_2$ pincer-type complexes

SUPPORTING INFORMATION

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Note concerning combustion analysis data presented in the Experimental section: Crystalline samples of SOP_2 complexes are notable for their ability to retain solvent under vacuum. This can be observed by combustion analysis of samples that are otherwise spectroscopically pure and free of salts. As such, we invoke the presence of residual solvent in several samples and suggest that other deviations from the calculated compositions arise from this phenomenon.

NMRs of conversion of **8** to **9**

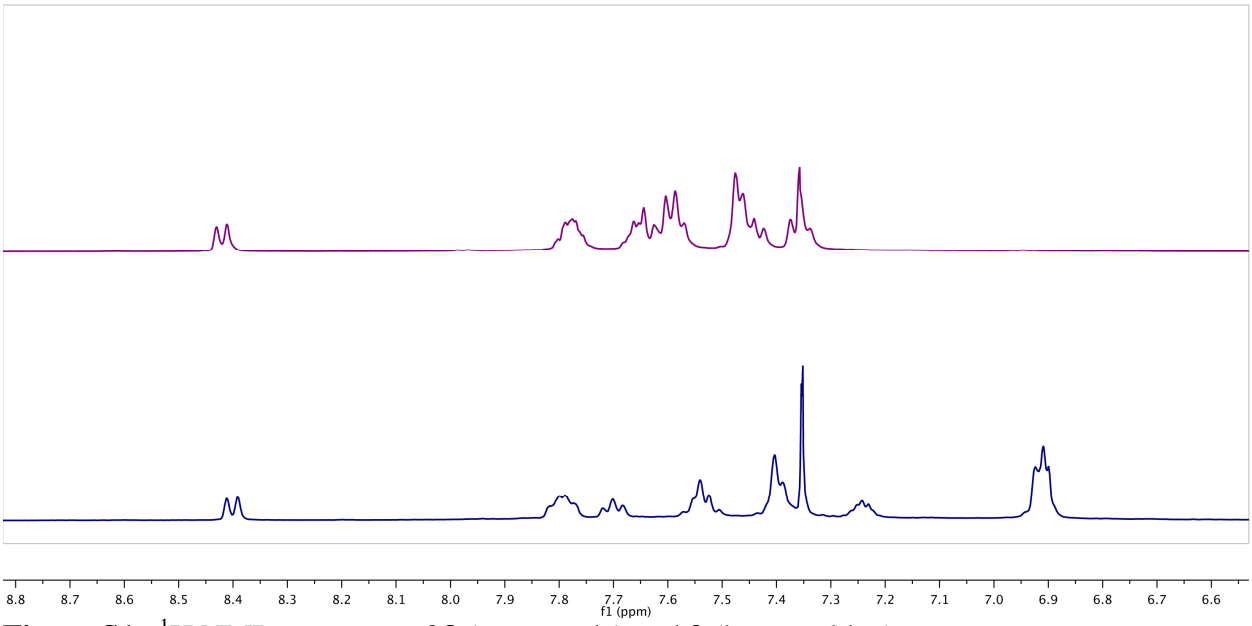

Figure S1. ^{1}H NMR spectrum of **8** (top, purple) and **9** (bottom, blue).

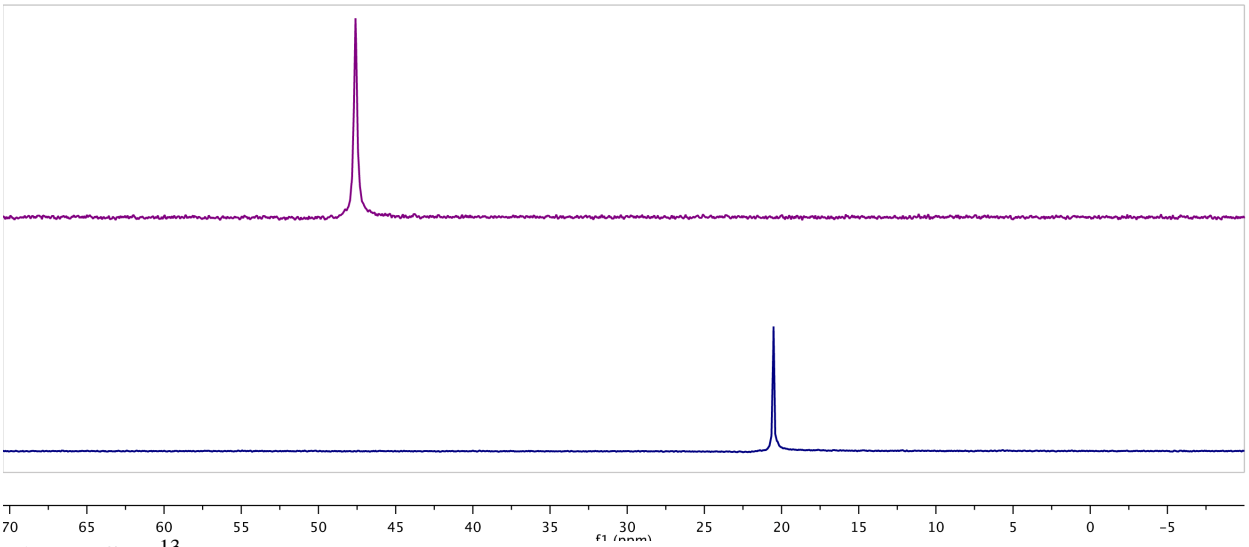

Figure S2. ^{13}P NMR spectrum of **8** (top, purple) and **9** (bottom, blue).

^{31}P and ^{195}Pt NMR simulations of **14**

Simulations were performed using the software package gNMR 5.0.6.[1] For the ^{31}P spectrum, initial guesses were provided for the chemical shifts and coupling constants and refined via several simulations. Final values were obtained by performing a least-squares fit to the experimental ^{31}P spectrum and are reported in the body of this article.

The ^{195}Pt chemical shift (-4,782 ppm) was simulated by performing a least-squares fit on the experimental spectrum using the $J_{P\text{-}Pt}$ values obtained from the simulation of the ^{31}P spectrum. The fit to the experimental data (see below) is highly satisfactory which provides independent support of the ^{31}P simulation.

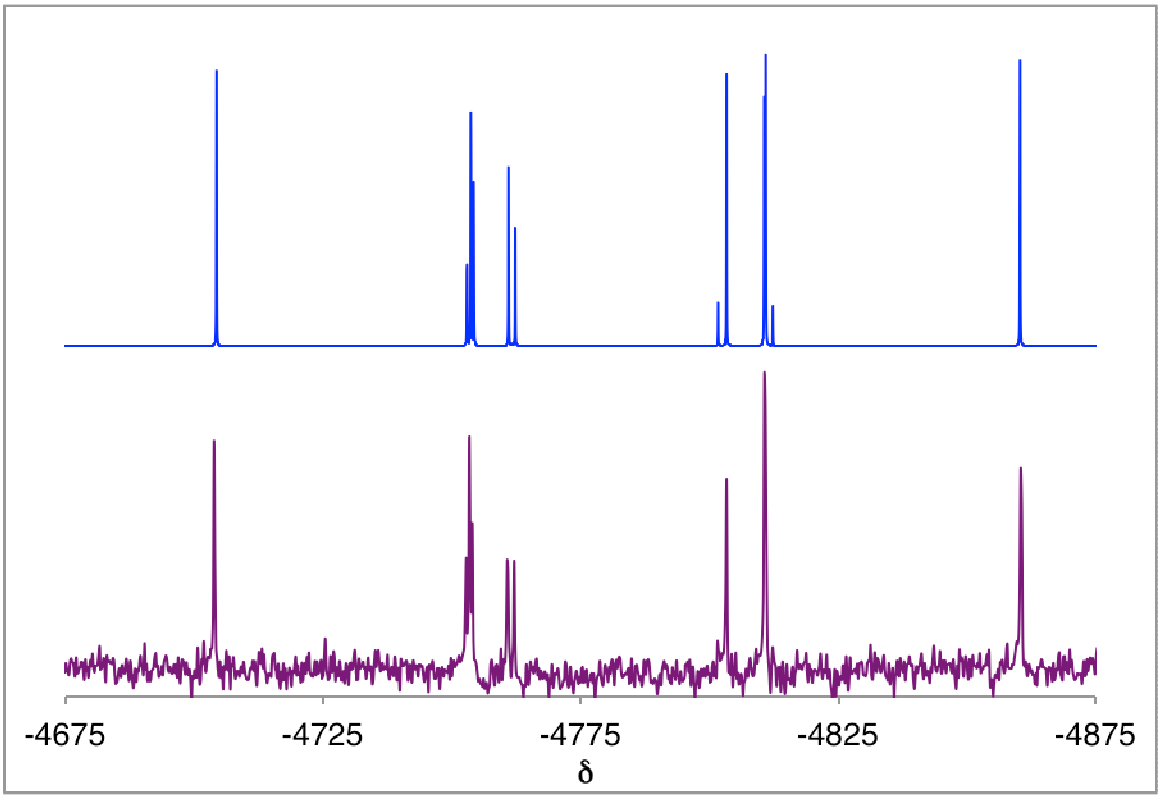

Figure S3. Simulated (top) and experimental (bottom) ^{195}Pt NMR spectra of **14** (86 MHz, CD_2Cl_2). Values used as input for simulation: $J_{PA\text{-}Pt} = 4244$ Hz, $J_{PB\text{-}Pt} = 4238$ Hz, $J_{PC\text{-}Pt} = 4917$ Hz.

[1] Budzelaar , P. H. M. Software may be downloaded free of charge at: http://home.cc.umanitoba.ca/~budzelaa/gNMR/gNMR.html

DFT calculations

All calculations were performed using the Gaussian03 software package.[2] The B3LYP functional and 6-311+g** basis set with the LANL2DZ effective core potential for Ir, P, S, and Cl atoms. Initial geometries were taken from x-ray crystallography coordinates and optimized which resulted in very slight geometrical changes. Orbital pictures were generated using the Gaussview program.[3]

[2] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[3] GaussView, Version 5, Roy Dennington, Todd Keith and John Millam, *Semichem Inc*., Shawnee Mission KS, 2009

X-ray Crystallography

Low-temperature x-ray diffraction data were collected on a Bruker Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, respectively), performing φ-and ω-scans. The structures were solved by direct or Patterson methods using SHELXS[4] and refined against $F2$ on all data by full- matrix least squares with SHELXL-97.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Tables S1 – S18 convey essential sample and refinement information and are paired with images to aid the reader in compound identification; full information on bond lengths, atomic coordinates, solvent molecules, etc. can be found in the accompanying cif file. All refinements were entirely straightforward with the following exceptions:

3: Two of the three THF molecules were modeled by a conformational disorder of the ring.
6: Two of the eight carbon atoms in the bound cyclooctene ring were modeled by a conformational disorder of the ring.
11: An ether molecule is disorded about an inversion center.
13: A THF molecule was modeled by a conformational disorder of the ring.
14: A CH_2Cl_2 molecule lies on an inversion center.
17: A CH_3CN molecule is disorder over two positions. The PF_6 anion is disorder about an F–P–F axis.
19: The PF_6 anion is disorder about an F–P–F axis.
21: The absolute structure parameter refined to 0.5 which indicates that the crystal was perfectly twinned to contain both enantiomeric forms.

[4] Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467-473.
[5] Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

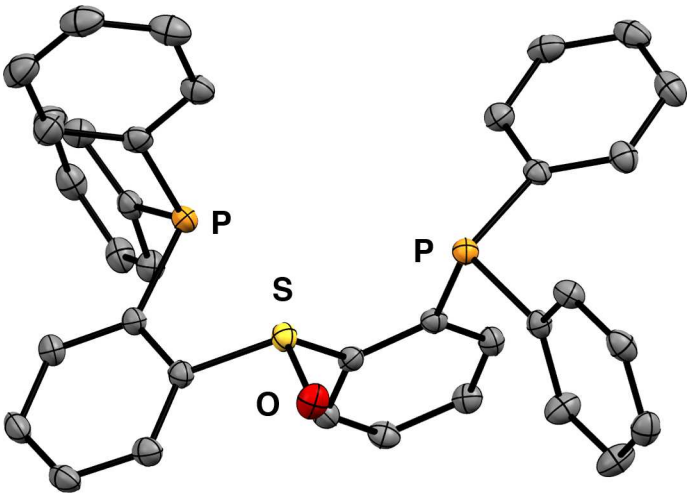

Table S1. Crystal data and structure refinement for **2**.

Identification code	SOP2	
Empirical formula	C36 H28 O P2 S	
Formula weight	570.58	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 10.3898(11) Å	α= 90°.
	b = 16.0613(19) Å	β= 90°.
	c = 34.037(4) Å	γ = 90°.
Volume	5679.9(11) $Å^3$	
Z	8	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	2384	
Crystal size	0.30 x 0.30 x 0.20 mm^3	
Theta range for data collection	1.20 to 29.57°.	
Index ranges	-14<=h<=14, -22<=k<=22, -47<=l<=47	
Reflections collected	121249	
Independent reflections	7980 [R(int) = 0.0672]	
Completeness to theta = 29.57°	100.0 %	
Max. and min. transmission	0.9506 and 0.9272	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7980 / 0 / 361	

Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1050
R indices (all data)	R1 = 0.0540, wR2 = 0.1137
Largest diff. peak and hole	0.460 and -0.362 e.$Å^{-3}$

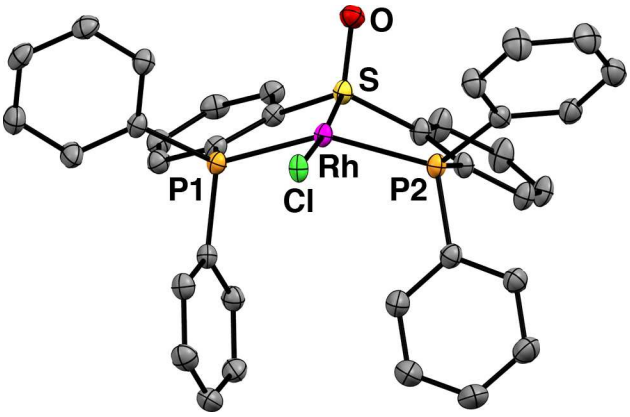

Table S2. Crystal data and structure refinement for **3** • 3 THF.

Identification code	(SOP2)RhCl	
Empirical formula	C48 H60 Cl O4 P2 Rh S	
Formula weight	933.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 16.9653(17) Å	α= 90°.
	b = 10.9952(11) Å	β= 108.588(2)°.
	c = 24.222(2) Å	γ = 90°.
Volume	4282.5(7) $Å^3$	
Z	4	
Density (calculated)	1.448 Mg/m^3	
Absorption coefficient	0.629 mm^{-1}	
F(000)	1952	
Crystal size	0.30 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.29 to 29.57°.	
Index ranges	-23<=h<=23, -15<=k<=15, -33<=l<=33	
Reflections collected	93917	
Independent reflections	12021 [R(int) = 0.0769]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9692 and 0.8336	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12021 / 553 / 543	
Goodness-of-fit on F^2	1.048	

Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1200
R indices (all data)	R1 = 0.0650, wR2 = 0.1335
Largest diff. peak and hole	1.622 and -0.925 e.Å^{-3}

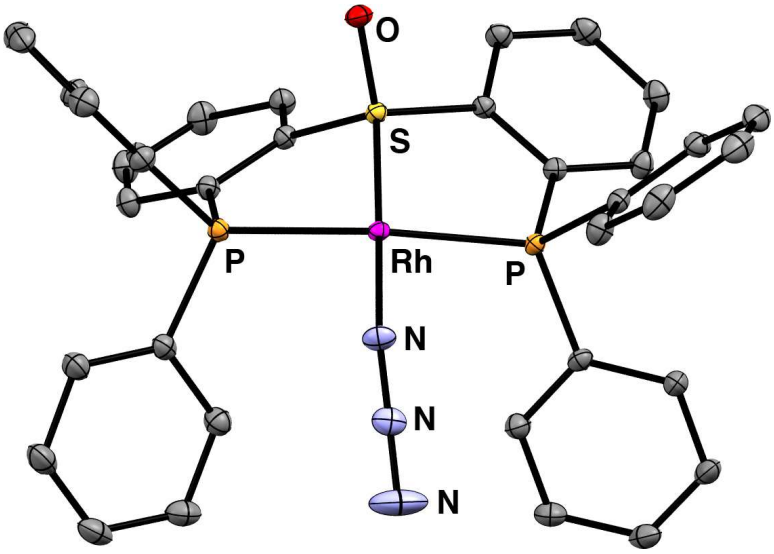

Table S3. Crystal data and structure refinement for **4**.

Identification code	(SOP2)RhN3	
Empirical formula	C36 H28 N3 O P2 Rh S	
Formula weight	715.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.0674(4) Å	α= 90°.
	b = 12.7353(4) Å	β= 90°.
	c = 19.5111(6) Å	γ = 90°.
Volume	2998.50(17) $Å^3$	
Z	4	
Density (calculated)	1.585 Mg/m^3	
Absorption coefficient	0.782 mm^{-1}	
F(000)	1456	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.91 to 36.35°.	
Index ranges	-20<=h<=19, -21<=k<=21, -32<=l<=32	
Reflections collected	102598	
Independent reflections	14570 [R(int) = 0.0583]	
Completeness to theta = 36.35°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9259 and 0.8592	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14570 / 0 / 397
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0527
R indices (all data)	R1 = 0.0329, wR2 = 0.0551
Absolute structure parameter	-0.014(10)
Largest diff. peak and hole	0.545 and -0.603 e.$Å^{-3}$

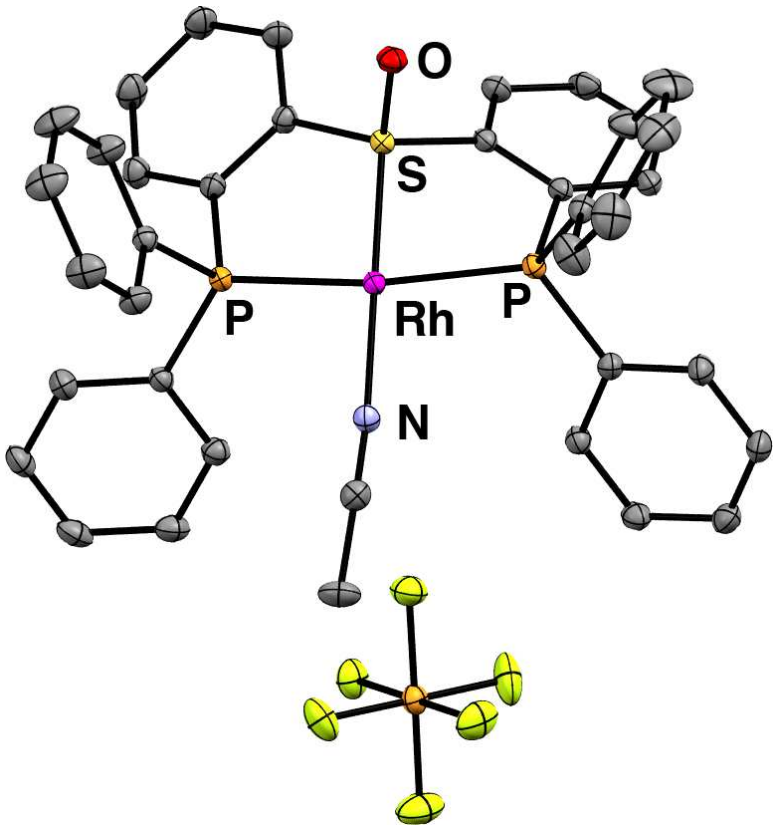

Table S4. Crystal data and structure refinement for **5** • 1.5 C7H8.

Identification code	[(SOP2)Rh(NCCH3)][PF6]	
Empirical formula	C48.50 H43 F6 N O P3 Rh S	
Formula weight	997.72	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.188(2) Å	α= 90°.
	b = 12.5088(7) Å	β= 125.157(2)°.
	c = 27.1062(16) Å	γ = 90°.
Volume	9200.0(9) $Å^3$	
Z	8	
Density (calculated)	1.441 Mg/m^3	
Absorption coefficient	0.582 mm^{-1}	
F(000)	4072	
Crystal size	0.3 x 0.1 x 0.08 mm^3	
Theta range for data collection	1.81 to 34.97°.	

Index ranges	-49<=h<=53, -19<=k<=19, -43<=l<=43
Reflections collected	129317
Independent reflections	20010 [R(int) = 0.0594]
Completeness to theta = 34.97°	99.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20010 / 508 / 559
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0787
R indices (all data)	R1 = 0.0586, wR2 = 0.0888
Extinction coefficient	none
Largest diff. peak and hole	1.299 and -0.692 e.$Å^{-3}$

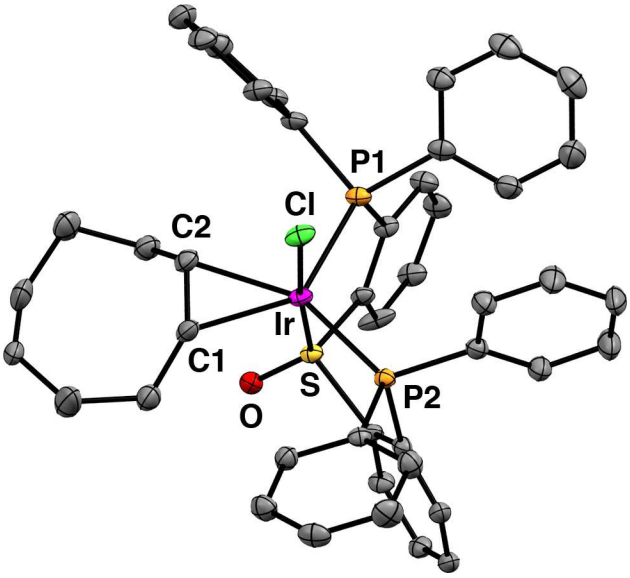

Table S5. Crystal data and structure refinement for **6** • 2 THF.

Identification code	(SOP2)IrCl(COE)	
Empirical formula	C52 H58 Cl Ir O3 P2 S	
Formula weight	1052.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8356(9) Å	α= 67.9740(10)°.
	b = 14.2555(12) Å	β= 87.4340(10)°.
	c = 17.2755(14) Å	γ = 67.8130(10)°.
Volume	2275.9(3) $Å^3$	
Z	2	
Density (calculated)	1.536 Mg/m^3	
Absorption coefficient	3.151 mm^{-1}	
F(000)	1068	
Crystal size	0.18 x 0.18 x 0.10 mm^3	
Theta range for data collection	1.28 to 28.70°.	
Index ranges	-14<=h<=14, -19<=k<=19, -23<=l<=23	
Reflections collected	48703	
Independent reflections	11715 [R(int) = 0.0648]	
Completeness to theta = 28.70°	99.5 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7435 and 0.6008
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11715 / 588 / 578
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0850
R indices (all data)	R1 = 0.0526, wR2 = 0.0917
Largest diff. peak and hole	4.086 and -1.163 e.$Å^{-3}$

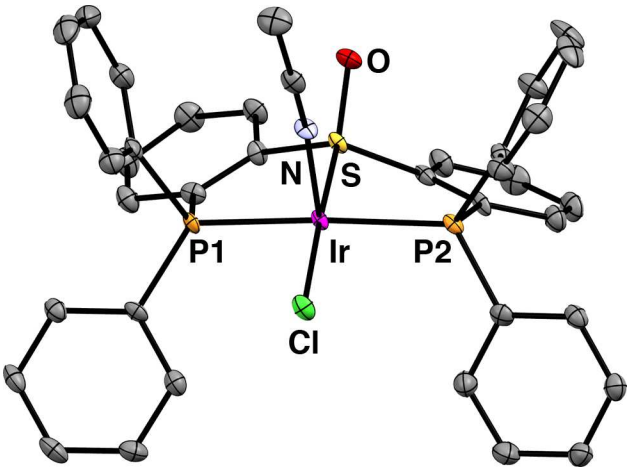

Table S6. Crystal data and structure refinement for **7** • CH3CN.

Identification code	[(SOP2)IrCl(H)(NCCH3)][OTf]	
Empirical formula	C41 H34 Cl F3 Ir N2 O4 P2 S2	
Formula weight	1029.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Pc	
Unit cell dimensions	a = 9.9455(4) Å	α= 90°.
	b = 13.7424(5) Å	β= 94.950(2)°.
	c = 15.6180(6) Å	γ = 90°.
Volume	2126.63(14) $Å^3$	
Z	2	
Density (calculated)	1.608 Mg/m^3	
Absorption coefficient	8.756 mm^{-1}	
F(000)	1018	
Crystal size	0.41 x 0.25 x 0.16 mm^3	
Theta range for data collection	3.22 to 66.59°.	
Index ranges	-11<=h<=11, -16<=k<=15, -18<=l<=18	
Reflections collected	36393	
Independent reflections	7298 [R(int) = 0.0368]	
Completeness to theta = 66.59°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3348 and 0.1237	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	7298 / 446 / 508
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0202, wR2 = 0.0504
R indices (all data)	R1 = NaN, wR2 = 0.0505
Absolute structure parameter	1.002(5)
Largest diff. peak and hole	0.848 and -0.616 e.$Å^{-3}$

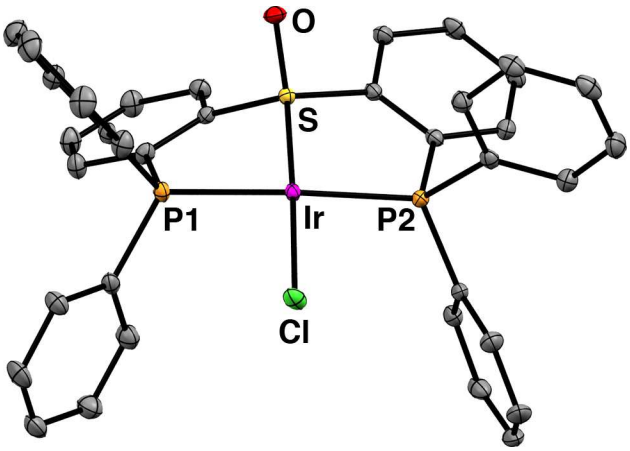

Table S7. Crystal data and structure refinement for **8** • THF.

Identification code	(SOP2)IrCl	
Empirical formula	C40 H36 Cl Ir O2 P2 S	
Formula weight	870.34	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1433(3) Å	α= 94.60°.
	b = 10.4097(3) Å	β= 92.44°.
	c = 17.6886(4) Å	γ = 113.23°.
Volume	1705.13(8) $Å^3$	
Z	2	
Density (calculated)	1.695 Mg/m^3	
Absorption coefficient	4.185 mm^{-1}	
F(000)	864	
Crystal size	0.23 x 0.15 x 0.06 mm^3	
Theta range for data collection	2.14 to 29.13°.	
Index ranges	-13<=h<=13, -14<=k<=14, -16<=l<=24	
Reflections collected	34905	
Independent reflections	9155 [R(int) = 0.0320]	
Completeness to theta = 29.13°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7874 and 0.4461	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9155 / 0 / 424	

Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0195, wR2 = 0.0466
R indices (all data)	R1 = 0.0211, wR2 = 0.0473
Largest diff. peak and hole	1.303 and -0.791 e.$Å^{-3}$

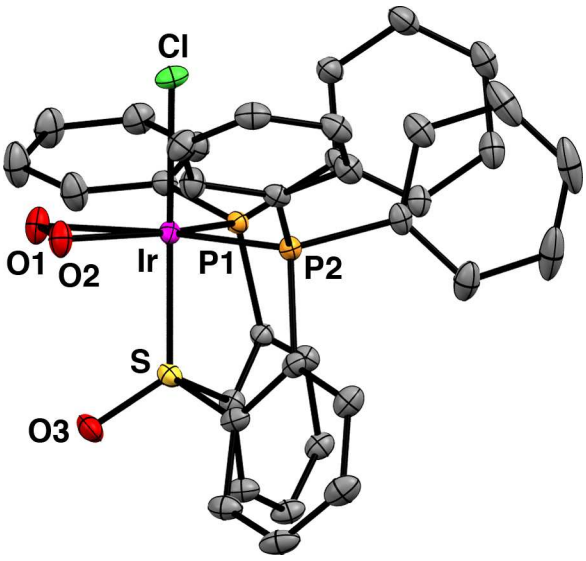

Table S8. Crystal data and structure refinement for **9**.

Identification code	(SOP2)Ir(Cl)(O2)	
Empirical formula	C36 H28 Cl Ir O3 P2 S	
Formula weight	830.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.1826(12) Å	α= 90°.
	b = 9.3648(7) Å	β= 104.127(2)°.
	c = 19.5299(14) Å	γ = 90°.
Volume	3047.5(4) $Å^3$	
Z	4	
Density (calculated)	1.810 Mg/m^3	
Absorption coefficient	4.680 mm^{-1}	
F(000)	1632	
Crystal size	0.22 x 0.07 x 0.06 mm^3	
Theta range for data collection	2.15 to 37.07°.	
Index ranges	-26<=h<=29, -15<=k<=15, -33<=l<=33	
Reflections collected	117710	
Independent reflections	15523 [R(int) = 0.0601]	
Completeness to theta = 37.07°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7665 and 0.4258	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15523 / 0 / 397
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0688
R indices (all data)	R1 = 0.0484, wR2 = 0.0747
Largest diff. peak and hole	7.405 and -2.049 e.$Å^{-3}$

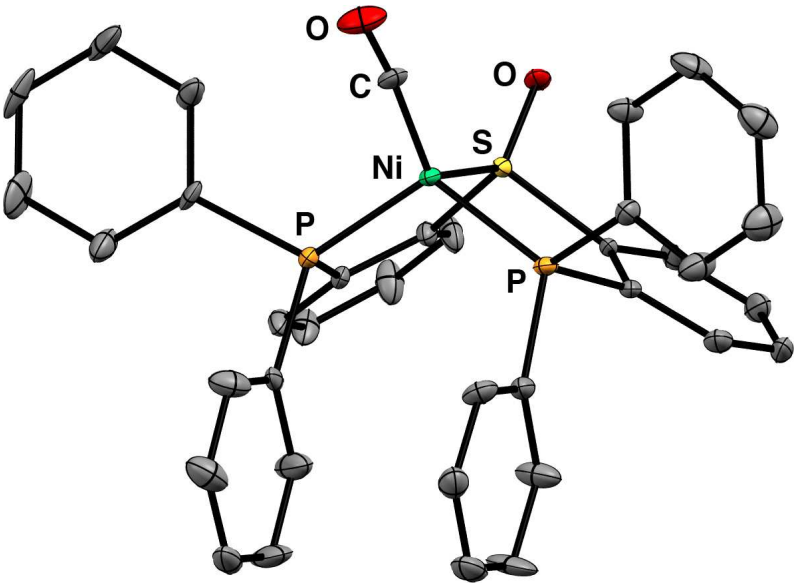

Table S9. Crystal data and structure refinement for **11** • 0.5 Et2O.

Identification code	(SOP2)Ni(CO)	
Empirical formula	C39 H28 Ni O2.50 P2 S	
Formula weight	689.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.1778(5) Å	α= 90°.
	b = 18.3139(9) Å	β= 104.693(3)°.
	c = 18.2294(9) Å	γ = 90°.
Volume	3286.8(3) $Å^3$	
Z	4	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.787 mm^{-1}	
F(000)	1424	
Crystal size	0.20 x 0.19 x 0.14 mm^3	
Theta range for data collection	2.07 to 26.37°.	
Index ranges	-12<=h<=12, -22<=k<=22, -22<=l<=22	
Reflections collected	90737	
Independent reflections	6723 [R(int) = 0.0544]	
Completeness to theta = 26.37°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8978 and 0.8584
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6723 / 430 / 433
Goodness-of-fit on F^2	1.326
Final R indices [I>2sigma(I)]	R1 = 0.0741, wR2 = 0.1778
R indices (all data)	R1 = 0.0805, wR2 = 0.1807
Largest diff. peak and hole	1.623 and -0.632 e.$Å^{-3}$

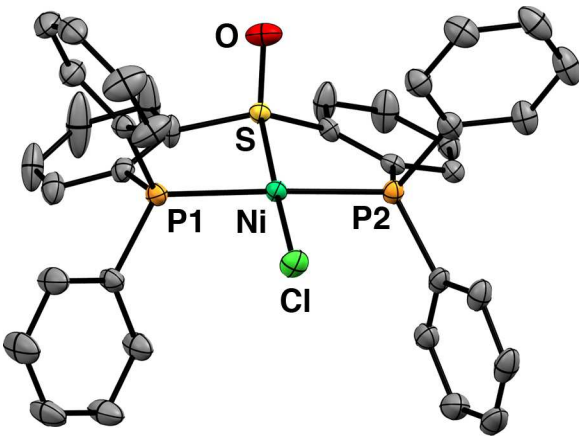

Table S10. Crystal data and structure refinement for **12** • C6H6.

Identification code	[(SOP2)NiCl][PF6]	
Empirical formula	C39 H31 Cl F6 Ni O P3 S	
Formula weight	848.77	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.3638(2) Å	α= 90°.
	b = 15.4106(2) Å	β= 106.0510(10)°.
	c = 18.3533(2) Å	γ = 90°.
Volume	3632.40(8) $Å^3$	
Z	4	
Density (calculated)	1.552 Mg/m^3	
Absorption coefficient	3.791 mm^{-1}	
F(000)	1732	
Crystal size	0.24 x 0.17 x 0.17 mm^3	
Theta range for data collection	3.44 to 65.08°.	
Index ranges	-15<=h<=15, -18<=k<=18, -19<=l<=21	
Reflections collected	68984	
Independent reflections	6189 [R(int) = 0.0320]	
Completeness to theta = 65.08°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5650 and 0.4631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6189 / 420 / 469	

Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0865
R indices (all data)	R1 = 0.0368, wR2 = 0.0888
Largest diff. peak and hole	0.817 and -0.643 e.$Å^{-3}$

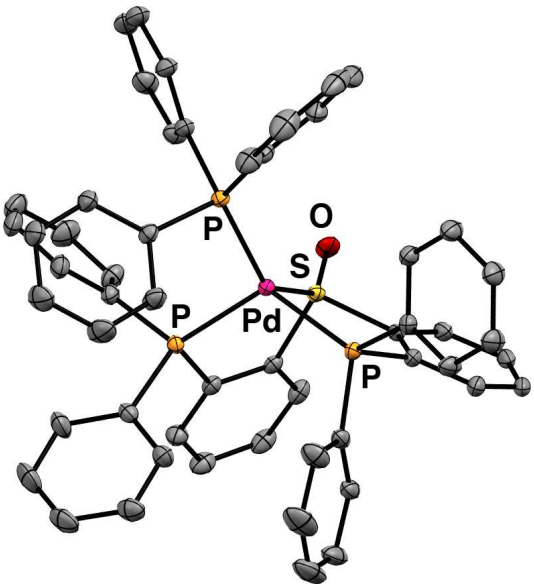

Table S11. Crystal data and structure refinement for **13** • THF • C6H6.

Identification code	(SOP2)Pd(PPh3)	
Empirical formula	C64 H57 O2 P3 Pd S	
Formula weight	101.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.0444(9) Å	α= 90°.
	b = 12.6952(6) Å	β= 99.7570(10)°.
	c = 20.6272(9) Å	γ = 90°.
Volume	5173.0(4) $Å^3$	
Z	4	
Density (calculated)	1.399 Mg/m^3	
Absorption coefficient	0.538 mm^{-1}	
F(000)	2256	
Crystal size	0.32 x 0.30 x 0.11 mm^3	
Theta range for data collection	1.89 to 33.73°.	
Index ranges	-31<=h<=30, -19<=k<=19, -32<=l<=32	
Reflections collected	181033	
Independent reflections	20653 [R(int) = 0.0591]	
Completeness to theta = 33.73°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.9432 and 0.8467
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20653 / 735 / 677
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1039
R indices (all data)	R1 = 0.0659, wR2 = 0.1152
Largest diff. peak and hole	1.590 and -1.231 e.$Å^{-3}$

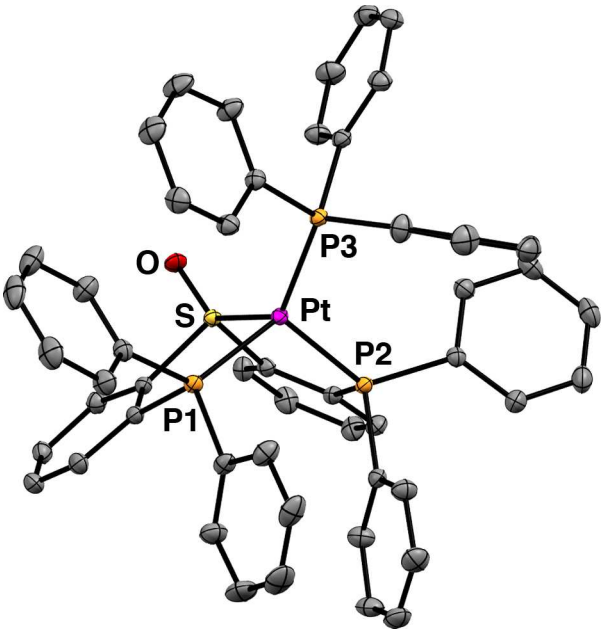

Table S12. Crystal data and structure refinement for **14** • CH2Cl2.

Identification code	(SOP2)Pt(PPh3)	
Empirical formula	C54.50 H43 Cl O P3 Pt S	
Formula weight	1069.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2946(5) Å	α= 86.456(2)°.
	b = 11.4688(5) Å	β= 88.538(2)°.
	c = 17.2693(8) Å	γ = 77.085(2)°.
Volume	2176.07(17) $Å^3$	
Z	2	
Density (calculated)	1.632 Mg/m^3	
Absorption coefficient	3.486 mm^{-1}	
F(000)	1068	
Crystal size	0.25 x 0.17 x 0.08 mm^3	
Theta range for data collection	1.85 to 36.43°.	
Index ranges	-18<=h<=18, -19<=k<=17, -28<=l<=28	
Reflections collected	112644	
Independent reflections	20303 [R(int) = 0.0404]	
Completeness to theta = 36.43°	95.5 %	

Max. and min. transmission	0.7679 and 0.4761
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	20303 / 0 / 568
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0545
R indices (all data)	R1 = 0.0322, wR2 = 0.0566
Largest diff. peak and hole	1.834 and -1.408 e.$Å^{-3}$

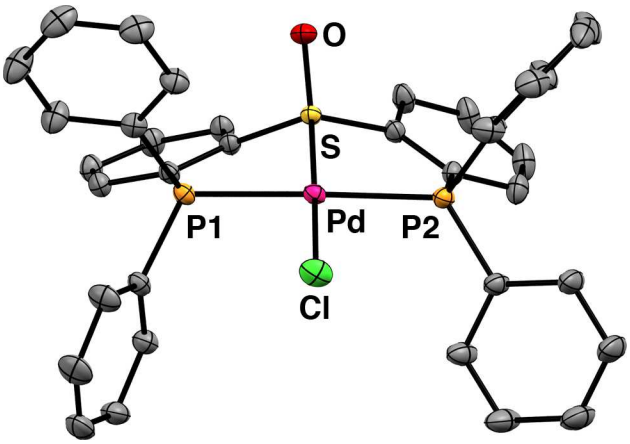

Table S13. Crystal data and structure refinement for **17** • CH3CN.

Identification code	[(SOP2)PdCl][PF6]	
Empirical formula	C38 H28 Cl F6 N O P3 Pd S	
Formula weight	895.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.3148(5) Å	α= 90°.
	b = 15.3494(5) Å	β= 105.973(2)°.
	c = 18.7144(6) Å	γ = 90°.
Volume	3677.1(2) $Å^3$	
Z	4	
Density (calculated)	1.617 Mg/m^3	
Absorption coefficient	0.828 mm^{-1}	
F(000)	1796	
Crystal size	0.22 x 0.20 x 0.11 mm^3	
Theta range for data collection	2.07 to 41.18°.	
Index ranges	-24<=h<=22, -28<=k<=28, -34<=l<=34	
Reflections collected	197055	
Independent reflections	24459 [R(int) = 0.0431]	
Completeness to theta = 41.18°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9144 and 0.8387	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	24459 / 588 / 525	

Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0853
R indices (all data)	R1 = 0.0518, wR2 = 0.0961
Largest diff. peak and hole	2.108 and -1.501 e.$Å^{-3}$

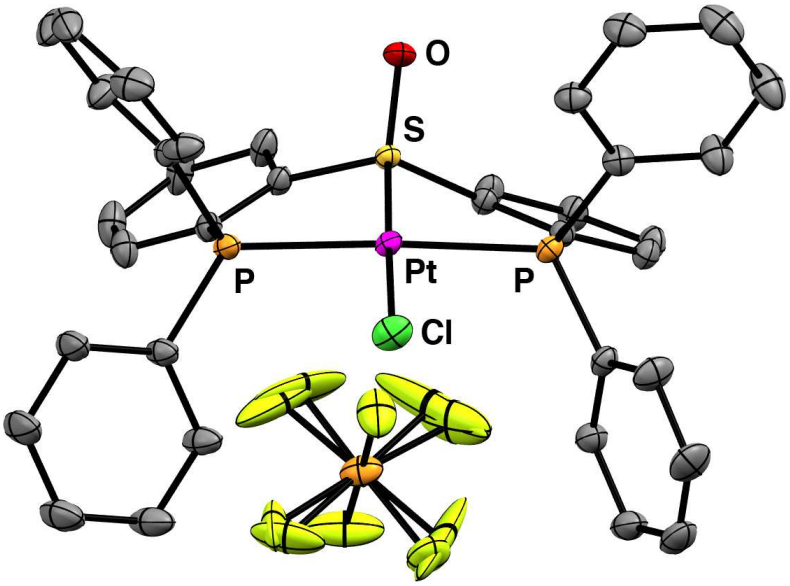

Table S14. Crystal data and structure refinement for **18** • CH3CN.

Identification code	[(SOP2)PtCl][PF6]	
Empirical formula	C38 H31 Cl F6 N O P3 Pt S	
Formula weight	987.15	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.3596(6) Å	α= 90°.
	b = 15.3077(7) Å	β= 106.112(2)°.
	c = 18.7872(9) Å	γ = 90°.
Volume	3691.2(3) $Å^3$	
Z	4	
Density (calculated)	1.776 Mg/m^3	
Absorption coefficient	4.124 mm^{-1}	
F(000)	1936	
Crystal size	0.33 x 0.25 x 0.15 mm^3	
Theta range for data collection	2.07 to 34.98°.	
Index ranges	-21<=h<=21, -24<=k<=24, -30<=l<=28	
Reflections collected	143041	
Independent reflections	16228 [R(int) = 0.0371]	
Completeness to theta = 34.98°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.5692 and 0.3466
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16228 / 575 / 507
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0234, wR2 = 0.0578
R indices (all data)	R1 = 0.0297, wR2 = 0.0608
Largest diff. peak and hole	2.825 and -1.569 e.$Å^{-3}$

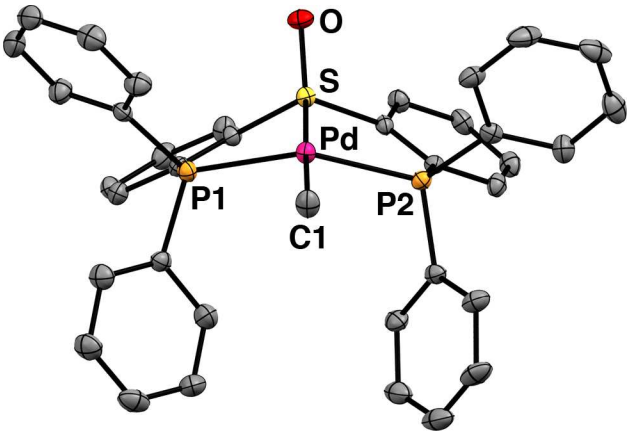

Table S15. Crystal data and structure refinement for **19** • 2 CH3CN.

Identification code	[(SOP2)Pd(CH3)][PF6]	
Empirical formula	C39 H34 F6 N O P3 Pd S	
Formula weight	878.04	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 14.2182(11) Å	α= 90°.
	b = 17.0580(13) Å	β= 104.462(2)°.
	c = 15.6882(12) Å	γ = 90°.
Volume	3684.4(5) $Å^3$	
Z	4	
Density (calculated)	1.583 Mg/m^3	
Absorption coefficient	0.755 mm^{-1}	
F(000)	1776	
Crystal size	0.50 x 0.50 x 0.15 mm^3	
Theta range for data collection	1.34 to 29.62°.	
Index ranges	-19<=h<=19, -23<=k<=23, -21<=l<=21	
Reflections collected	68041	
Independent reflections	20594 [R(int) = 0.0514]	
Completeness to theta = 29.62°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8952 and 0.7040	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20594 / 1 / 979	

Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0790
R indices (all data)	R1 = NaN, wR2 = 0.0831
Absolute structure parameter	1.042(12)
Largest diff. peak and hole	0.665 and -0.403 e.$Å^{-3}$

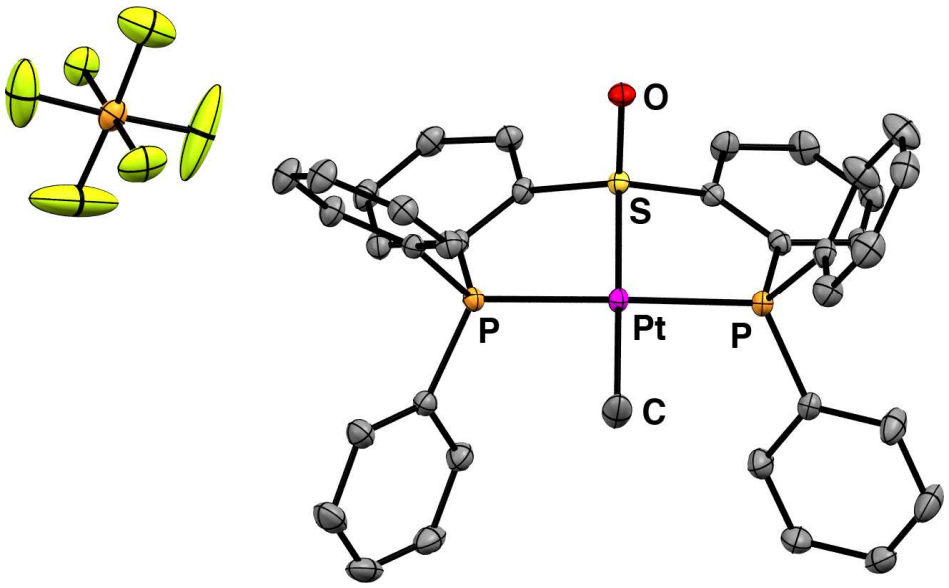

Table S16. Crystal data and structure refinement for **20** • CH3CN.

Identification code	[(SOP2)Pt(CH3)][PF6]	
Empirical formula	C39 H31 F6 N O P3 Pt S	
Formula weight	142.77	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.936(2) Å	α= 90°.
	b = 16.722(4) Å	β= 95.722(7)°.
	c = 25.078(6) Å	γ = 90°.
Volume	3728.4(15) $Å^3$	
Z	4	
Density (calculated)	1.717 Mg/m^3	
Absorption coefficient	4.011 mm^{-1}	
F(000)	1892	
Crystal size	0.45 x 0.45 x 0.25 mm^3	
Theta range for data collection	1.47 to 29.61°.	
Index ranges	-12<=h<=12, -23<=k<=23, -34<=l<=34	
Reflections collected	82043	
Independent reflections	10464 [R(int) = 0.0430]	
Completeness to theta = 29.61°	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.4337 and 0.2655
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10464 / 0 / 470
Goodness-of-fit on F^2	1.134
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0682
R indices (all data)	R1 = 0.0302, wR2 = 0.0694
Largest diff. peak and hole	1.731 and -1.422 e.$Å^{-3}$

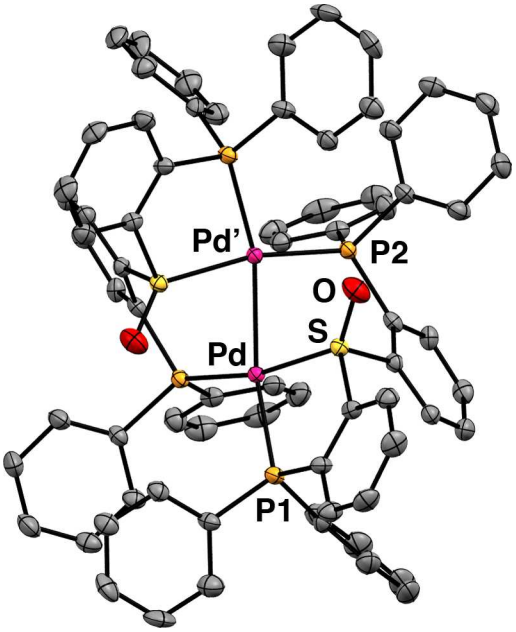

Table S17. Crystal data and structure refinement for **21** • 3 THF.

Identification code	[(SOP2)Pd]2[PF6]2	
Empirical formula	C84 H80 F12 O5 P6 Pd2 S2	
Formula weight	1860.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P3(2)21	
Unit cell dimensions	a = 14.9538(4) Å	α= 90°.
	b = 14.9538(4) Å	β= 90°.
	c = 30.2975(9) Å	γ = 120°.
Volume	5867.3(3) $Å^3$	
Z	3	
Density (calculated)	1.579 Mg/m^3	
Absorption coefficient	0.718 mm^{-1}	
F(000)	2838	
Crystal size	0.19 x 0.14 x 0.05 mm^3	
Theta range for data collection	1.71 to 24.11°.	
Index ranges	-17<=h<=16, -16<=k<=17, -34<=l<=34	
Reflections collected	45427	
Independent reflections	6173 [R(int) = 0.0489]	
Completeness to theta = 24.11°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9664 and 0.8757
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6173 / 0 / 502
Goodness-of-fit on F^2	1.095
Final R indices [I>2sigma(I)]	R1 = 0.0314, wR2 = 0.0743
R indices (all data)	R1 = 0.0359, wR2 = 0.0764
Absolute structure parameter	0.50(2)
Largest diff. peak and hole	1.367 and -0.275 e.$Å^{-3}$

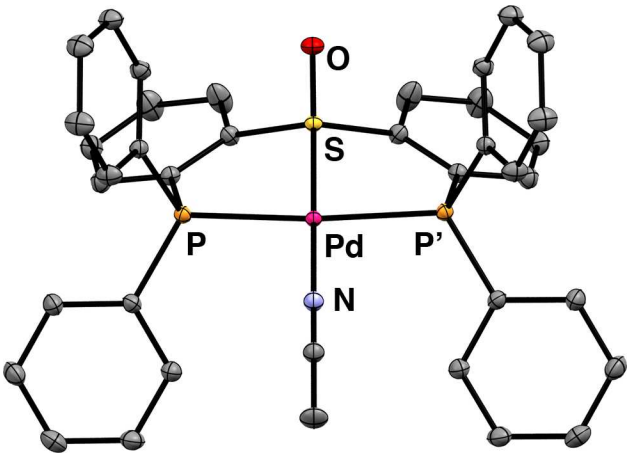

Table S18. Crystal data and structure refinement for **22** • 2 CH3CN.

Identification code	[(SOP2)Pd(NCCH3)][PF6]2	
Empirical formula	C42 H37 F12 N3 O P4 Pd S	
Formula weight	1090.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 17.8021(9) Å	α= 90°.
	b = 22.4724(12) Å	β= 90°.
	c = 11.0253(5) Å	γ = 90°.
Volume	4410.7(4) $Å^3$	
Z	4	
Density (calculated)	1.642 Mg/m^3	
Absorption coefficient	0.703 mm^{-1}	
F(000)	2192	
Crystal size	0.16 x 0.09 x 0.08 mm^3	
Theta range for data collection	2.06 to 37.80°.	
Index ranges	-30<=h<=30, -38<=k<=38, -19<=l<=18	
Reflections collected	181663	
Independent reflections	12056 [R(int) = 0.0717]	
Completeness to theta = 37.80°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9459 and 0.8959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12056 / 0 / 310	

Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0621
R indices (all data)	R1 = 0.0458, wR2 = 0.0689
Largest diff. peak and hole	1.125 and -0.787 e.$Å^{-3}$